

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/FI04/000797

International filing date: 23 December 2004 (23.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: FI
Number: 20031904
Filing date: 23 December 2003 (23.12.2003)

Date of receipt at the International Bureau: 03 March 2005 (03.03.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

Helsinki 8.2.2005

ETUOIKEUSTODISTUS
PRIORITY DOCUMENT



Hakija
Applicant

Kemira Oyj
Helsinki

Patenttihakemus nro
Patent application no

20031904

Tekemispäivä
Filing date

23.12.2003

Kansainvälinen luokka
International class

D21H

Keksinnön nimitys
Title of invention

"Method of modifying a lignocellulosic fibre product"
(Menetelmä lignoselluloosatuohteen muokkaamiseksi)

Täten todistetaan, että oheiset asiakirjat ovat tarkkoja jäljennöksiä Patentti- ja rekisterihallitukselle alkuaan annetuista selityksestä, patenttivaatimuksista, tiivistelmästä ja piirustuksista.

This is to certify that the annexed documents are true copies of the description, claims, abstract and drawings, originally filed with the Finnish Patent Office.

Marketta Tehikoski
Apulaistarkastaja

Maksu 50 €
Fee 50 EUR

Maksu perustuu kaupp- ja teollisuusministeriön antamaan asetukseen 1142/2004 Patentti- ja rekisterihallituksen maksullisista suoritteista muutoksineen.

The fee is based on the Decree with amendments of the Ministry of Trade and Industry No. 1142/2004 concerning the chargeable services of the National Board of Patents and Registration of Finland.

Osoite:	Arkadiankatu 6 A	Puhelin:	09 6939 500	Telefax:	09 6939 5328
	P.O.Box 1160	Telephone:	+ 358 9 6939 500	Telefax:	+ 358 9 6939 5328
	FI-00101 Helsinki, FINLAND				

METHOD OF MODIFYING A LIGNOCELLULOSIC FIBRE PRODUCT

Background of the Invention

5 Field of the Invention

The present invention relates to fibrous products. In particular, the present invention concerns a process for reducing the susceptibility of lignocellulosic material to unwanted brightness reversion, in particular to brightness reversion caused by light or heat.

10

Description of Related Art

It is well-known in the art that light (UV light in particular), heat, moisture and chemicals can give rise to changes in the brightness of cellulose pulps. Usually, such changes result in reduced reflectivity, particularly in blue light. This phenomenon is known as brightness reversion or yellowing and can be caused by various factors depending on which type of pulp is concerned. Heat and damp are the main causes of the brightness reversion of chemical (lignin-free) pulps, whereas mechanical pulps mostly yellow when they are exposed to light. The brightness reversion of mechanical pulps also varies depending on the raw material (type of wood), production method (with or without chemical pretreatment), and after-treatment (bleaching with different reagents) used. Thus, for instance, sulphonation and peroxide bleaching greatly increase the susceptibility of pulp to light-induced yellowing.

25 The brightness reversion of lignocellulosic pulps and products made from such pulps can be reduced or even prevented in various ways, for instance by means of impregnation or surface treatment using UV screens, antioxidants, or polymers, or by coating the surface with a coating layer or a layer of non-yellowing chemical pulp. Various additives are described in the patent literature. Thus, US 4,978,363 discloses a composition and method for treating fibers based on a mixture of an organopolysiloxane having at least one amino-substituted hydrocarbon radical directly bonded to a silicon atom and a higher fatty carboxylic acid. The carboxylic acid reacts with the amino radicals to reduce yellowing and oxidation of the fiber treatment. The composition and method provide non-yellowing

30

fibers and a treatment agent that does not gel during use, such as when exposed to carbon dioxide and/or used to treat carbon fibers.

US 6,599,326 discloses inhibition of pulp and paper yellowing using hydroxylamines and
5 other coadditives. Chemical pulps or papers, especially kraft pulps or papers, which may still contain traces of lignin, have enhanced resistance to yellowing when they contain an effective stabilizing amount of a N,N-dialkylhydroxylamine, an ester, amide or thio substituted N,N-dialkylhydroxylamine or N,N-dibenzylhydroxylamine or an ammonium salt thereof. This performance is often further enhanced by the presence of one or more
10 coadditives selected from the group consisting of UV absorbers, polymeric inhibitors, nitrones, fluorescent whitening agents and metal chelating agents. Combinations of hydroxylamines or their salts, benzotriazole or benzophenone UV absorbers and a metal chelating agent are, according to the cited patent, considered particularly effective. As specific examples, the patent mentions N,N-diethylhydroxylamine and N,N-dibenzyl-
15 hydroxylamine.

Many of the additives that have been found to prevent yellowing are expensive or problematic from an environmental point of view; others are only effective when introduced in so large amounts that they may have a negative effect on other properties of
20 the product or be uneconomical. Accordingly, there is still a need for methods of preventing yellowing

Summary of the Invention

25 It is an aim of the present invention to eliminate the problems of the prior art and to provide a new method of reducing or preventing yellowing. The method aims at effectively reducing both light- and heat-induced brightness reversion of mechanical pulps and high-yield chemical pulps.

30 The invention is based on the finding that the reactions that take place during oxidation, in particular enzymatic oxidation, of lignin appear to be similar to the reactions that cause brightness reversion. Therefore, the initial reaction causing brightness reversion can be activated by enzymatic means and simultaneously immediately blocked by targeted functionalization, by retarding or stopping the reactions.

Thus, the present invention provides a method of modifying fibres by bonding of new compounds to the oxidized fibres via radical pathways. In particular, the aim of the bonding of the compounds is to stabilize the structure by forming a colourless lignin derivative unable to participate in yellowing reactions.

According to the invention, new fibrous products with modified properties are produced by activating the fibres of the matrix with an oxidizing agent capable of oxidizing phenolic or similar structural groups, which may undergo reactions conducive to the formation of coloured sites on the fibres, and attaching to the oxidized sites at least one modifying agent to block the reactivity of the oxidized sites. The activation is preferably carried out enzymatically.

The modifying agent has at least one functional site or reactive structure, which provides for binding of the modifying compound to the lignocellulosic fibre material, in particular at the oxidized phenolic groups or corresponding chemical structures of the fibres, which have been oxidized during the activation step.

Based on the above, the present invention provides a process for producing a fibre material having increased resistance to brightness reversion, comprising a lignocellulosic fibrous matrix with phenolic or similar structural groups and a modifying agent reducing the susceptibility of yellowing, including the steps of

- reacting the lignocellulosic fibrous matrix with an oxidizing agent in the presence of a catalyst capable of catalyzing the oxidation of phenolic or similar structural groups by said oxidizing agent to provide an oxidized fibre material, and
- contacting the oxidized fibre material with a modifying agent containing at least one first functional site, which is capable of bonding to oxidized fibre material, said modifying agent being capable of imparting to the lignocellulosic fibre material improved resistance to brightness reversion caused by light or heat or combinations thereof.

Another embodiment of the invention provides a method of reducing light or heat induced brightness reversion of mechanical or high-yield chemical pulp, comprising the steps of enzymatically oxidizing phenolic groups of the pulp and bonding to the oxidized phenolic groups a substance capable of forming a colourless lignin derivative unable to participate in yellowing reactions.

More specifically, the present invention is mainly characterized by what is stated in the characterizing parts of claims 1 and 14.

The present invention provides important advantages. Importantly, the invention makes it possible to produce novel kinds of fibrous materials having improved brightness reversion. By means of the process, the modifying agents can be reliably attached to the fibres, and the improved resistance to yellowing will not be significantly impaired by, e.g., extensive washing of the fibres prior to forming the material into a paper or cardboard web.

Further details and advantages of the invention will become apparent from the following detailed description and the appended working examples.

Brief Description of the Drawings

Figure 1 depict in graphical form yellowing of spruce TMP samples as function of irradiation energy.

Detailed Description of the Invention

As mentioned above, the invention generally relates to a method of producing fibre compositions with reduced susceptibility to yellowing.

The fibre matrix comprises fibres containing phenolic or similar structural groups, which are capable of being oxidized by suitable oxidizing agents. Such fibres are typically "lignocellulosic" fibre materials, which include fibre made of annual or perennial plants or wooden raw material by, for example, mechanical, chemimechanical or chemical pulping. During industrial refining of wood by, e.g., refiner mechanical pulping (RMP), pressurized refiner mechanical pulping (PRMP), thermomechanical pulping (TMP), groundwood

(GW) or pressurized groundwood (PGW) or chemithermomechanical pulping (CTMP), a woody raw material, derived from different wood species as for example hardwood and softwood species, is refined into fine fibres in processes, which separate the individual fibres from each other. The fibres are typically split between the lamellas along the interlamellar lignin layer, leaving a fibre surface, which is at least partly covered with lignin or lignin-compounds having a phenolic basic structure

Within the scope of the present invention, also chemical pulps are included if they are susceptible to brightness reversion and have a residual content of lignin sufficient to give at least a minimum amount of phenolic groups necessary for providing binding sites for the modifying agent. Generally, the concentration of lignin in the fibre matrix should be at least 0.1 wt-%, preferably at least about 1.0 wt-%.

In addition to paper- and paperboard-making pulps of the above kind, also other kinds of fibres of plant origin can be treated, such as bagasse, jute, flax and hemp.

An essential feature of the invention is to block brightness reversion by modifications of phenolic hydroxyls, alfa-carbonyls and/or alfa-hydroxyls on the fibres. In particular, by subjecting lignin structures to enzymatic oxidation to yield oxidized groups of the aforesaid kind, the normal reactions causing brightness reversion can be attained. These reactions are then stopped by bonding a desired compound to the activated, oxidized groups.

In the first stage of the present process, the lignocellulosic fibre material is reacted with a substance capable of catalyzing the oxidation of phenolic or similar structural groups to provide an oxidized fibre material. Typically, the substance is an enzyme and the enzymatic reaction is carried out by contacting the lignocellulosic fibre material with an oxidizing agent, which is capable – in the presence of the enzyme – of oxidizing the phenolic or similar structural groups to provide an oxidized fibre material. Such oxidizing agents are selected from the group of oxygen and oxygen-containing gases, such as air, and hydrogen peroxide. Oxygen can be supplied by various means, such as efficient mixing, foaming, gases enriched with oxygen or oxygen supplied by enzymatic or chemical means, such as peroxides to the solution. Peroxides can be added or produced in situ.

According to an embodiment of the invention, the oxidative enzymes capable of catalyzing oxidation of phenolic groups, are selected from, e.g. the group of phenoloxidases (E.C.1.10.3.2 benzenediol:oxygen oxidoreductase) and catalyzing the oxidation of o- and p-substituted phenolic hydroxyl and amino/amine groups in monomeric and polymeric aromatic compounds. The oxidative reaction leads to the formation of phenoxy radicals. Another groups of enzymes comprise the peroxidases and other oxidases. "Peroxidases" are enzymes, which catalyze oxidative reaction using hydrogen peroxide as their electron acceptor, whereas "oxidases" are enzymes, which catalyze oxidative reactions using molecular oxygen as their electron acceptor.

10

In the method of the present invention, the enzyme used may be for example laccase, tyrosinase, peroxidase or oxidase, in particular, the enzyme is selected from the group of laccases (EC 1.10.3.2), catechol oxidases (EC 1.10.3.1), tyrosinases (EC 1.14.18.1), bilirubin oxidases (EC 1.3.3.5), horseradish peroxidase (EC 1.11.1.7), manganase peroxidase (EC1.11.1.13) and lignin peroxidase (EC 1.11.1.14).

15

The amount of the enzyme is selected depending on the activity of the individual enzyme and the desired effect on the fibre. Advantageously, the enzyme is employed in an amount of 0.0001 to 10 mg protein/g of dry matter fiber.

20

Different dosages can be used, but advantageously a dosage of about 1 to 100,000 nkat/g, more advantageously 10-500 nkat/g.

The activation treatment is carried out in a liquid medium, preferably in an aqueous medium, such as in water or an aqueous solution, at a temperature in the range of 5 to 100 °C, typically about 10 to 85 °C. Normally, a temperature of 20-80°C is preferred. The consistency of the pulp is, generally, 0.5 to 95 % by weight, typically about 1 to 50 % by weight, in particular about 2 to 40 % by weight. The pH of the medium is preferably slightly acidic, in particular the pH is about 2 to 10, in the case of phenoloxidases.

25

Peroxidases are typically employed at pH of about 3 to 12 . The reaction mixture is stirred during oxidation. Other enzymes can be used under similar conditions, preferably at pH 2-10.

30

In the second step of the process, a modifying agent capable of reducing the susceptibility to yellowing of lignocellulosic fibres is bonded to the oxidized phenolic or similar structural groups of the matrix. Such a modifying agent typically exhibits at least one first functional site, which is compatible with the fibrous matrix, and at least one second functional site or structure providing for the above technical effect, as will be explained in more detail below.

The first functional site comprises in particular functional groups, which are capable of contacting and binding to the fibre at the oxidized phenolic or similar structural groups or at its vicinity. The bond formed between the oxidized phenolic or similar residue can be covalent or ionic or even based on hydrogen bonding. Typical functionalities of the first functional site include reactive groups, such as hydroxyl (including phenolic hydroxy groups), carboxy, anhydride, aldehyde, ketone, amino, amine, amide, imine, imidine and derivatives and salts thereof, to mention some examples. Also electronegative bonds, such as carbon-to-carbon double bonds, carbon-to-hetero atom (e.g. $C=N$, $C=O$) as well as oxo or azo -bridges can provide for bonding to the oxidized residues.

It is essential that modifying agent is chemically or physically bonded to the fibre matrix to such an extent that at least an essential part of it cannot be removed. One criterion, which can be applied to test this feature, is washing in aqueous medium, because often the fibrous matrix will be processed in an aqueous environment, and it is important that it retains the new and valuable properties even after such processing. Thus, preferably, at least 10 mol-%, in particular at least 20 mol-%, and preferably at least 30 mol-%, of the modifying agent remains attached to the matrix after washing or leaching in an aqueous medium.

According to an embodiment of the invention, the modifying agent is activated with an oxidizing agent.

The interaction of the oxidized lignocellulosic material and the modifying agent, resulting in bonding of the modifying agent to the lignocellulosic material, typically takes place in liquid phase, usually in water or in another aqueous medium. The pulp or other lignocellulosic fibrous matrix is suspended in the medium and it is contacted with the modifying agent or a precursor thereof, which is dissolved or dispersed in the same medium. The conditions can vary freely, although it is preferred to carry out the contacting

- under mixing or stirring. The temperature is generally between the melting point and the boiling point of the medium; preferably it is about 5 to 100 °C. Depending on the modifying agent or its precursor, the pH of the medium can be neutral or weakly alkaline or acidic (pH typically about 2 to 12). It is preferred to avoid strongly alkaline or acidic conditions because they can cause hydrolyzation of the fibrous matrix. Normal pressure (ambient pressure) is also preferred, although it is possible to carry out the process under reduced or elevated pressure in pressure resistant equipment. Generally, the consistency of the fibrous material is about 0.5 to 95 % by weight during the contacting stage.
- 10 According to a particularly preferred embodiment, the first and the second stages of the process are carried out in the same reaction medium, without separating the fibrous matrix after the oxidation step. The conditions (consistency, temperature, pH, pressure) can, though, even in this embodiment be different during the various processing stages.
- 15 The first and the second stages of the process are carried out sequentially or simultaneously

According to one preferred embodiment, the modifying agent is an aliphatic or aromatic, monocyclic, bicyclic or tricyclic substance. The aliphatic compound can be an unsaturated carboxylic acid, advantageously a monocarboxylic unsaturated fatty acid, having 4 to 30 carbon atoms. In particular, the modifying agent can be a monocarboxylic, unsaturated fatty acids containing a minimum of two double bonds, preferably two conjugated double bonds. Such fatty acids have an even number of carbon atoms, typically in the range of 16 to 22.

- 25 Examples of suitable compounds include linoleic and linolenic acid. It would appear that the unsaturated fatty acid bonds to the oxidized groups or structure via one of the double bonds.

Other suitable compounds include antioxidants, such as tocopherol and beta-carotene.

- 30 The compound can have special properties, such as capability to trap radicals and form colourless substituents.

The above two steps can be carried sequentially or simultaneously. Also other compounds, such as papermaking chemicals may be present during the reaction steps.

After the above processing, the modified fibre having new properties is generally separated
5 from the liquid reaction and further used in target applications.

The following non-limiting example illustrates the invention:

Example 1

10 A 5 g portion of bleached spruce TMP was suspended in water. The pH of the suspension was adjusted to pH 4.5 by addition of acid. The suspension was stirred at RT. Laccase dosage was 1000 nkat/g of pulp dry matter and the final pulp consistency was 7.5 %. After 30 minutes laccase reaction, 0.15 mmol linoleic acid/g of pulp dry matter was added to the
15 pulp suspension. After 1 h total reaction time, the pulp suspension was filtered and the pulp was washed thoroughly with water. Handsheets were prepared. For comparison purposes, reference treatments were carried out using the same procedure as described above but without addition of laccase or linoleic acid or both. The light-fastness on the pulps was tested with Xenotest 150S light exposure and weathering test instrument using "window
20 glass" filter. The brightness of the handsheets was measured as function of irradiation dosage. The results are presented graphically in Fig. 1.

From the results presented in Fig. 1, it is apparent that the addition of linoleic acid and laccase was found to decrease the yellowing tendency of the pulp. In other words, addition
25 of a modifying agent in the presence of an oxidizing agent and a suitable catalyst, the yellowing tendency of pulp was decreased.

Example 2

Bonding of new compounds to TMP

30

A 5 g portion of spruce TMP was suspended in water. The pH of the suspension was adjusted to pH 4.5 by addition of acid. The suspension was stirred at RT. Laccase dosage was 1000 nkat/g of pulp dry matter and the final pulp consistency was 7.5 %. After 30 minutes laccase reaction the new compound was added to the pulp suspension. After 1 h

- total reaction time, the pulp suspension was filtered and the pulp was washed thoroughly with water. Handsheets were prepared. For comparison purposes, reference treatments were carried out using the same procedure as described above but without addition of laccase or the new compound. The light-fastness on the pulps was tested with Xenotest 5 150S light exposure and weathering test instrument using "window glass" filter. The changes in the ISO brightnesses after irradiation are summarized in Table 1.

Table 1

Treatment	Irradation (Whm ²)	Δ brigtness (as ISO- Brightness)
TMP Reference	1260	10
TMP + laccase + ferulic acid (0.15 mmol/g)	1260	3
TMP + laccase + vinyl laurate (0.3 mmol/g)	1260	2

Claims

1. A process for producing a fibre material having reduced susceptibility to yellowing, comprising a lignocellulosic fibrous matrix with phenolic or similar structural groups and a modifying agent, said process comprising the steps of
 - reacting the lignocellulosic fibrous matrix with an oxidizing agent in the presence of a enzyme capable of catalyzing the oxidation of phenolic or similar structural groups by said oxidizing agent to provide an oxidized fibre material, and
 - contacting the oxidized fibre material with a modifying agent containing at least one first functional portion, which is compatible with the oxidized fibre material, said modifying agent being capable of providing the lignocellulosic fibre material with properties reducing susceptibility to yellowing.
2. The process according to claim 1, wherein the modifying agent is activated with an oxidizing agent.
3. The process according to claim 1, wherein the modifying agent is a brightness reversion inhibitor.
4. The process according to claims 1 to 3, wherein the modifying agent is selected from the group comprising unsaturated carboxylic acids, monocarboxylic unsaturated fatty acids, and monocarboxylic unsaturated fatty acids containing a minimum of two double bonds, preferably two conjugated double bonds.
5. The process according to claim 4, wherein the modifying agent is linoleic acid or linolenic acid.
6. The process according to claim 1 or 2, wherein the modifying agent is selected from the group of antioxidants.

7. The process according to any of the preceding claims, wherein the enzyme capable of catalyzing the oxidation of phenolic or similar structural groups is selected from the group of peroxidases and oxidases.
- 5 8. The process according to claim 7, wherein the enzyme is selected the group of laccases (EC 1.10.3.2), catechol oxidases (EC 1.10.3.1), tyrosinases (EC 1.14.18.1), bilirubin oxidases (EC 1.3.3.5), horseradish peroxidase (EC 1.11.1.7), manganase peroxidase (EC 1.11.1.13) and lignin peroxidase (EC 1.11.1.14).
- 10 9. The process according to any of the preceding claims, wherein the enzyme dosage is about 1 to 100,000 nkat/g, preferably 10-500 nkat/g, and it is employed in an amount of 0.0001 to 10 mg protein/g of dry matter.
- 15 10. The process according to any of the preceding claims, wherein the oxidizing agent is selected from the group of oxygen, hydrogen peroxide and oxygen-containing gases, such as air.
11. The process according to any of the preceding claims, wherein oxygen or oxygen-containing gas is introduced into the aqueous slurry during the reaction.
- 20 12. The process according to any of the preceding claims, wherein the reaction of step (a) is carried out in an aqueous or dry phase at a consistency of 1 to 95 % by weight of the fibre material.
- 25 13. The process according to any of the preceding claims, wherein the reaction is carried out at temperature 5-100° C
14. Method of reducing light or heat induced brightness reversion of mechanical or high-yield chemical pulp, comprising the steps of
- 30 - enzymatically oxidizing phenolic groups of the pulp and
- bonding to the oxidized phenolic groups a substance capable of forming a colourless lignin derivative unable to participate in yellowing reactions.

15. The process according to any of the preceding claims, wherein the reaction steps are carried out sequentially or simultaneously.

(57) Abstract

The present invention concerns a process for reducing the susceptibility of lignocellulosic material to unwanted yellowing, particularly yellowing caused by light and heat. According to the invention, the fibres are activated enzymatically and then contacted with a modifying agent capable of bonding to the oxidized fibre material, rendering the lignocellulosic fibre material improved resistance to brightness reversion.

By means of the invention, brightness reversion caused by light or heat or a combination thereof can be retarded and even stopped.

L 7

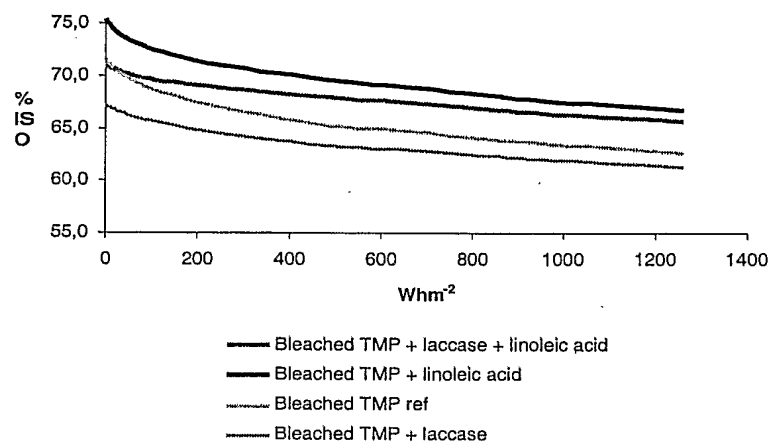


Fig. 1. Yellowing (ISO brightness) of spruce TMP samples as function of irradiation energy.